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Synthesis and Characterization of Photoluminescent PVA/ZnS: Mn^{2+} Nanocomposites

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Abstract

A ZnS nanoparticle doped with Mn2+ is synthesized in aqueous media and PVA using chemical co-precipitation method. This colloid was analyzed using uv-vis spectrophotometry. It is observed that the absorption peak blue shifts as compared to the bulk absorption of ZnS suggesting the nanoparticle formation. The energy gaps of these nanoparticles were calculated from the uv-vis spectra. The average particle size analysis is carried out using XRD. Photoluminescence of PVA/ ZnS:Mn^{2+} is studied. It is observed that the composite sample exhibits an orange emission peak as is reported for pure ZnS: Mn^{2+}.

Keywords: Nanoparticles, ZnS: Mn^{2+}, XRD, Photoluminiscence

1. Introduction

Luminescent nanoparticles with advantageous properties for optoelectronics applications are available in both inorganic and organic forms. In recent years a wide range of materials including metals, semiconductors and metal oxides are synthesized in nanometer scale. In particular II–VI semiconductor nanocrystals (NCs) are receiving a lot of attention due to their potential application in optoelectronics and photonics. The colour tunability

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of these semiconductor nanoparticles as a function of size is one of their most attractive properties. But a lot of issues needs to be addressed before it can be brought to end use. In that sense, the current bottle-neck of these materials is their poor compatibility with micropatterning methods in general and MEMS processes in particular. Inorganic nanoparticles dispersed in polymer matrix may lead to versatile nanoscale devices. Colloidal methods provide effective routes to prepare semiconductor nanoparticles that are dispersible in organic solvents. Recently the focus is towards the fabrication of polymer nanocomposites containing micrometer or nanometer sized inorganic semiconductor. This is due to the good processability and the structural properties of the polymeric matrix, and the unique optoelectronic characteristics of the inorganic moiety which can be used for many purposes such as optical switches, sensors, electro-luminescent devices, lasers and biomedical tags. Inorganic semiconductor nanocrystals (NCs), primarily based on CdSe/ZnS, are highly efficient light-emitters in the visible range of the spectrum. These nanoparticles when integrated with polymers can lead to a lot of applications [1-4].

The incorporation of inorganic particles into polymers allows one to integrate new functions inside polymer matrices. Modification of the matrix by dispersing a second inorganic component into the polymer typically results in a significant loss of transparency due to scattering from large particles or agglomerates. Incorporation of smaller particle sizes can restore the transparency of the polymer selected as well as add new functionalities to the polymer composite. The general method adopted is to prepare the composites using in-situ polymerization techniques in a solution containing the particle dispersion. Here we have chosen a simple as prepared partially crystalline PVA which is a water soluble polymer as the matrix without reverting to the traditional *insitu* synthesis technique.

2. Experimental

Nanoparticles of Mn^{2+}-doped ZnS were prepared by chemical co-precipitation method. All the chemicals were of AR grade. Freshly prepared aqueous solutions of the chemicals were used for the synthesis of nanoparticles. These particles were prepared at room

temperature by dropping simultaneously 20 ml of 0.4 M solution of zinc sulphate, 20 ml of 0.1 M solution of manganese sulphate and 20 ml of 0.5 M solution of sodium sulphide into 40 ml of distilled water containing 20 ml of 0.1 M solution of EDTA which was vigorously stirred using a magnetic stirrer. The role of EDTA was to stabilize the particles against aggregation of particles. The precipitate was separated from the reaction mixture, washed several times with distilled water. The wet precipitate was dried and thoroughly ground [5]. The same procedure is used to synthesize ZnS nanoparticles without Manganese doping. XRD of the Mn^{2+} doped sample were carried out to know the average particle size.

90/10 (wt/wt) composition of PVA/ ZnS: $Mn2^{+}$ is prepared for the experimental purpose. 5 wt% of PVA solution was prepared. Nanoparticles of (Mn^{2+} approximately 10% concentrations) doped ZnS were prepared by chemical co-precipitation method as mentioned above and added to the PVA solution. The solution was kept for stirring for a day. The final solution was poured into a petridish and kept for drying. The film of the sample was obtained after a week of drying. Undoped ZnS in PVA matrix was also prepared.

3. Results and discussion

3.1 XRD Analysis

Fig. 1 shows the XRD pattern of the sample ZnS doped with Mn^{2+}. The XRD pattern contain broad peak at $2\theta = 28.2^{o}$ indicating the formation of nanostructure. Using the Debye Scherrer formula

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where θ is the Bragg's angle, λ is the Cu-Kα radiation wavelength, β is the full width at half maxima, (here K = 0.89 for spherical shape) the mean crystalline size (D) was calculated. The particles were assumed to be spherical. The calculated size is found to be 3.8 nm. There are three diffraction peaks corresponding to diffraction angle 2θ of 28.28^{o}, 47.84^{o} and 55.98^{o} corresponding to (002), (110) and (112) lattice planes of hexagonal ZnS respectively.

The small changes in diffraction angle are clearly a result of lattice contraction that is expected to occur because of higher surface to volume ratio [6].

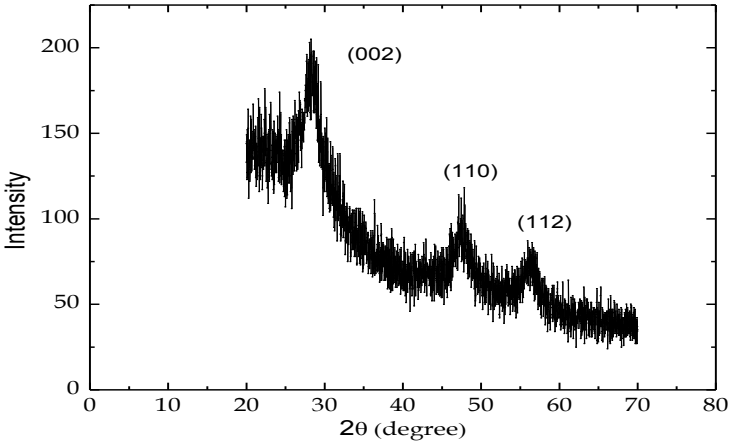

Fig. 1. XRD pattern of ZnS: Mn^{2+} sample

3.2. Optical studies

The optical absorption of the samples is shown. The optical absorbances were recorded at the room temperature using UV-VIS spectrophotometer. The sample shows the peak at a wavelength 330 nm for pure ZnS, suggesting blue shift w.r.t. the bulk arising from quantum confinement effect in the nanoparticles. The absorption peak corresponding to the doped sample and the composites with PVA are listed in the Table 1.

The band gap of bulk ZnS is 3.68 eV at 300 K. The fundamental absorption, which corresponds to the transmission from valence band to the conduction band, is employed to determine the band gap of the material. The relation between absorption coefficient (α) and incident photon energy (hν) can be written as

$$\alpha = A\left(h\nu - E_g\right)^n / h\nu$$

where A is a constant and E_g is the band gap of the material. Exponent 'n' depends on the type of the transition; n may have

values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. But in the nanocrystalline sample, there may be some deviation from the bulk like transition. From the above equation, it is clear that, plot of $(\alpha h\nu)^2$ vs $h\nu$ will indicate a divergence at an energy value E_g where the transition takes place. Taking the values at discontinuities as the band gap, the nature of the transition (i.e., the n value) is determined. The exact value of the band gap is determined by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs $h\nu$ graph to the $h\nu$ axis [7]. The values calculated using the above procedure is also tabulated in Table 1.

Sample	Absorption Maxima (nm)	Energy Gap (eV)
ZnS	330	3.2
ZnS:Mn^{2+}	250	4.3
PVA/ZnS	320	3.2
PVA/ZnS: Mn^{2+}	340	3.2

Table 1: Energy gap and peak wavelength of the samples

3.3. Photoluminescence studies

Photoluminescence (PL) spectra for the samples were recorded using (JY Fluorolog-3-11) spectroflurometer. The PVA/ ZnS: Mn^{2+} nanocomposite samples are photoexcited at 320 nm. Subsequent transfer of electron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn^{2+} in ZnS. PL spectrum of composite contains an orange emission lying between 590-600 nm. The composite has a peak similar to pure ZnS: $Mn2^{+}$ nanoparticles [8, 9].

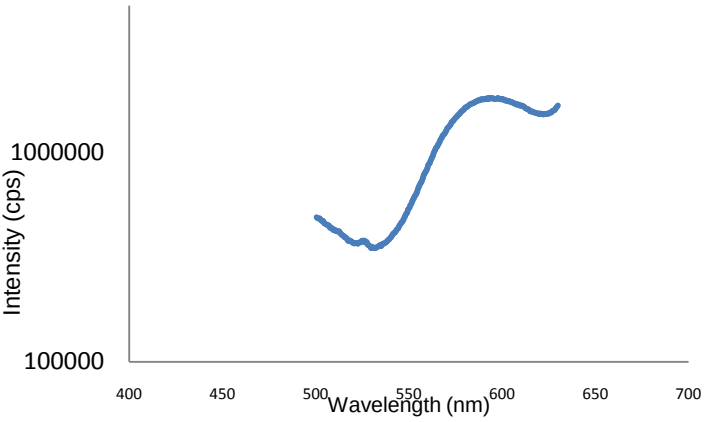

Fig. 2. Photoluminescence spectra of PVA/ ZnS: Mn2+ nanocomposite.

4. Conclusion

ZnS, ZnS:Mn^{2+}, PVA/ZnS and PVA/ZnS:Mn^{2+} were synthesized by chemical co-precipitation method. The band gap of the samples was determined by UV-VIS spectra analyses. XRD analysis shows the ZnS sample prepared is in a hexagonal phase. The particle size is found to be 3.85 nm. The composite shows an emission in the orange region as the ZnS: $Mn2^{+}$ samples.

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